TRACE GAS CONCENTRATIONS IN SMALL STREAMS OF THE GEORGIA PIEDMONT

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Abstract. We have been measuring concentrations of the trace gases nitrous oxide (N_2O), methane (CH_4), and carbon dioxide (CO_2) and other parameters in 17 headwater streams within the South Fork Broad River (SFBR) watershed on a monthly basis since January 2001. Land use within each watershed was calculated from the National Land Cover Data (NLCD) database. The concentrations of all three gases have varied widely over the course of the study, and have frequently (N_2O) or always (CH_4 and CO_2) exceeded levels expected if the streams were in equilibrium with atmospheric concentrations of these gases. Streams draining highly developed watersheds have the highest N_2O and CO_2 concentrations and streams draining pasture-dominated watersheds have the highest CH_4 concentrations. Streams draining forested watersheds have the lowest N_2O, CO_2, and CH_4 concentrations. The concentrations of all three of these trace gases exhibit significant positive correlations with dissolved organic carbon (DOC) and total dissolved nitrogen (TDN) concentrations suggesting that they may be useful indicators of organic waste and/or nutrient inputs to streams. In some cases, elevated stream trace gas concentrations may serve as early warning indicators of watershed disturbance.

INTRODUCTION

There is great interest in the effects of watershed land use on in-stream nutrient concentrations and cycling (e.g., Jones et al., 2001). Because of their shallow depths and high surface-to-volume ratios, headwater streams frequently exhibit high rates of nutrient cycling (Peterson et al., 2001). First- and second-order streams are a critical part of the overall river network, comprising ~ 95% of the total number of stream channels and 73% of the total stream channel length in the US (Meyer and Wallace, 2001). Because of their importance in the river network and high rates of biogeochemical cycling, headwater streams provide valuable ecosystem services by reducing transport of various pollutants to downstream ecosystems such as rivers and lakes (Meyer and Wallace, 2001). Because of their small size, their ecosystem function is easily impaired by human disturbance of their catchment, riparian zone, and channel (Meyer and Wallace, 2001). Given their importance in providing ecosystem services within the overall river network and their vulnerability to disturbance, greater protection of headwater streams seems justified. Effective protection of headwater streams will require improved understanding of factors within their watersheds that alter their function.

The extent to which the concentrations of biologically reactive trace gases such as N_2O, CO_2, and CH_4 deviate from equilibrium with the atmosphere can provide useful indication of the rate of organic matter decomposition and of the overall nature of the aquatic metabolism (e.g., anoxic vs. aerobic). Because organic matter processing is one of the useful ecosystem services provided by streams, and stream ecosystem function can be impaired by excess inputs of organic wastes, trace gas concentrations could provide valuable information about stream ecosystem function to water quality managers and regulators.

The atmospheric concentrations of N_2O, CO_2, and CH_4 have increased substantially since the beginning of the industrial era. All three are important greenhouse gases and together account for most of the atmospheric temperature forcing attributed to anthropogenic gas emissions. In addition, N_2O is an important contributor to stratospheric ozone depletion. Agricultural development and land use change have made major contributions to the atmospheric increases of all three gases, although their budgets are still quite uncertain. The objective of this research is to develop easily measured indicators of stream ecosystem function and response to stressors such as excess organic waste and nutrients.

STUDY AREA

The Broad River is located in northeast Georgia and flows from the Appalachian mountains to its confluence with the Savannah River. The SFBR is a tributary of the Broad River that is 128 km in length. The SFBR is located in the southwest part of the Broad River watershed and drains an area of about 556 km^2 mostly within Oglethorpe and Madison counties. The SFBR watershed is primarily rural and remains in a largely undeveloped state. Agriculture is the main land use throughout the valley and also includes some managed forests. Industrial use in the watershed is mainly limited to a few granite quarries. The human population growth rates of Oglethorpe and Madison counties during the last decade were above the state average. Effective methods to assess the impact of the accompanying residential development on stream function are needed.

METHODS

Seventeen headwater watersheds within the SFBR watershed ranging from 0.5 to 3.4 km^2 were selected. We have been monitoring concentrations of trace gases, nutrients (nitrate, nitrite, ammonium, orthophosphate, dissolved organic nitrogen and phosphorus, total nitrogen and phosphorus) and other parameters (temperature, conductivity, dissolved oxygen, alkalinity, pH, DOC, flow rate) on an approximately monthly basis since January 2002 at the outlets of the watersheds. Trace gas concentrations are determined by partitioning the dissolved gas into a gas phase within a syringe by an equilibration technique (Elkins, 1980), followed by measuring gas concentrations with a gas chromatograph equipped with an electron capture detector and thermal conductivity detector, and then applying appropriate solubility constants (Weiss and Price, 1980; Wiesenburg and Guinasso, 1979).

Percentages of forested land, agricultural and pasture land, residential areas, wetlands and open water surfaces within each watershed were calculated from the NLCD database. The study sites were then classified as either forested, agricultural and pasture land, residential/developed or mixed land use depending on the land uses observed within the watershed.

RESULTS AND DISCUSSION

Mean discharge and water temperature in the sampling sites ranged from 1.5 to 17.5 L s^{-1} and from 19 to 24 ºC respectively. All the streams were slightly acid, with mean pH around 6.5 or lower, and most of then showed low alkalinity (less than 40 mg $CaCO_3$ L^{-1}). Stream dissolved oxygen concentrations reached levels as low as 20% of saturation in some of the streams during the low flow and high temperature conditions of summer. Mean N_2O, CO_2, CH_4, DOC, and TDN concentrations and land use within the watersheds are shown in Table 1. Individual N_2O concentrations varied widely from about 10 nM (atmospheric equilibrium concentration) to greater than 150 nM. Mean N_2O concentrations in the streams range from slightly supersaturated to a factor of six supersaturated with respect to atmospheric N_2O. IndividualCO_2 concentrations varied from about 30 to 600 μM (3 to 50 supersaturated relative to the atmosphere). Mean CO_2 concentrations in the streams are supersaturated relative to the atmosphere by factors ranging from about 7 to 40. Individual CH_4 concentrations range from <0.002 to 25 μM (up to 12,500 supersaturated relative to the atmosphere). Mean CH_4 concentrations in the streams are supersaturated relative to the atmosphere by factors ranging from about 100 to 5000. These high levels of supersaturation indicate that, in at least some watersheds, headwater streams may be a significant source of trace gases to the atmosphere.

Grouping the streams by land use in their watersheds suggests that those draining highly developed watersheds have the highest mean dissolved N_2O and CO_2 concentrations although the differences are statistically significant only for comparisons with the forested and mixed land use watersheds. The group of streams draining pasture-dominated watersheds had a significantly higher mean CH_4 concentration than any of the other stream groups draining the other land use types. The stream with the greatest percentage of pasture land use of those studied (P38), and a large number of cattle with direct access to the stream in its watershed, has by far the largest mean CH_4 concentration, the largest mean TDN concentration, and the second highest mean DOC concentration (Table 1). The impact of pasture land use on stream chemistry is likely to be highly variable as many areas that are classified as pasture from remote sensing data are hayfields that are not directly grazed by animals. Other areas classified as pasture support many animals, often with direct stream access, and receive large inputs

Table 1. Mean concentrations of N_2O, CO_2, CH_4, DOC, and TDN in SFBR headwater streams

Site[a]	%F	%R	%P	N_2O (nM)[b]	CO_2 (μM)	CH_4 (μM)	DOC (mg L^{-1})	TDN (mg L^{-1})
F30	80.0	<0.1	19.0	13.5 " 3.8	108 " 51	0.9 " 0.3	1.2 " 0.7	0.2 " 0.1
F47	85.8	<0.1	13.8	43.7 " 8.3	213 " 39	1.0 " 0.3	0.9 " 0.5	0.3 " 0.2
F71	83.9	2.0	10.7	15.4 " 3.1	91 " 20	0.5 " 0.2	1.3 " 1.1	0.3 " 0.1
P8	22.2	<0.1	76.6	29.1 " 14.2	192 " 45	3.0 " 2.0	3.6 " 1.4	1.4 " 0.9
P31	30.3	<0.1	69.2	28.8 " 7.8	109 " 22	1.4 " 0.7	2.4 " 0.9	1.3 " 0.2
P38	10.8	<0.1	88.9	46.1 " 15.2	279 " 78	10.1 " 5.8	4.9 " 2.7	4.3 " 4.9
P43	34.5	<0.1	65.4	20.6 " 7.8	125 " 35	0.9 " 0.6	1.5 " 0.7	0.8 " 0.2
M7	42.0	0.2	57.7	23.5 " 12.7	154 " 40	1.2 " 0.6	1.8 " 0.6	0.7 " 0.4
M10	67.0	2.0	30.9	15.7 " 3.3	75 " 26	1.3 " 0.7	2.2 " 0.8	0.7 " 0.3
M58	46.5	18.1	35.0	17.6 " 4.8	74 " 31	0.4 " 0.3	0.9 " 0.6	0.9 " 0.4
M61	35.8	19.4	44.4	19.4 " 4.8	109 " 33	0.5 " 0.2	1.5 " 0.7	0.8 " 0.1
M63	27.6	7.3	64.3	20.3 " 4.4	88 " 32	0.2 " 0.1	0.7 " 0.7	1.2 " 0.1
M78	33.8	3.4	62.0	62.6 " 37.1	397 " 121	3.8 " 1.9	3.3 " 1.3	1.0 " 0.2
R6	40.3	36.5	21.9	63.1 " 19.0	260 " 59	2.0 " 1.0	3.2 " 0.8	2.9 " 0.7
R28	55.4	25.3	17.9	24.2 " 6.0	109 " 38	0.6 " 0.3	1.2 " 0.7	0.6 " 0.1
R40	49.9	24.0	25.1	13.6 " 4.2	169 " 72	1.2 " 0.5	1.4 " 0.6	0.2 " 0.1
R79	45.5	36.6	17.8	46.2 " 19.8	353 " 71	2.6 " 3.2	6.0 ".1.6	3.5 " 1.3

a: F - forested, R - residential/developed, P - pasture/agriculture; b: numbers following " are one standard deviation

of feed and fertilizer, often in the form of poultry litter. Streams draining forested watersheds had the lowest N_2O, CO_2, and CH_4 concentrations.

Many of the streams that drain watersheds with substantial residential or pasture land uses exhibit elevated DOC and TDN concentrations compared to streams draining forested watersheds (Table 1). Elevated stream DOC and TDN levels probably reflect inputs of organic wastes from septic systems and/or animal agriculture and fertilizer. The impact of residential land use on stream chemistry is likely to be highly variable and depend on factors such as the concentration and proximity of the development to the stream as well as septic system effectiveness.

The mean stream concentrations of N_2O, CO_2, and CH_4 all exhibited significant positive linear correlations with mean stream DOC concentration (Figure 1), with R^2 of 0.40, 0.58 and 0.54, respectively. Mean stream concentrations of N_2O, CO_2, and CH_4 also exhibited significant positive linear correlations with mean stream TDN concentration, with R^2 of 0.37, 0.34, and 0.57, respectively. The positive relationships between stream trace gas concentrations and DOC and TDN concentrations suggest that trace gas concentrations could be useful indicators of organic waste contamination of streams. In most cases, elevated stream trace gas concentrations were accompanied by elevated levels of DOC and/or TDN. In the case of one stream from a forested watershed (F47), elevated N_2O and CO_2 concentrations were not accompanied by elevated DOC

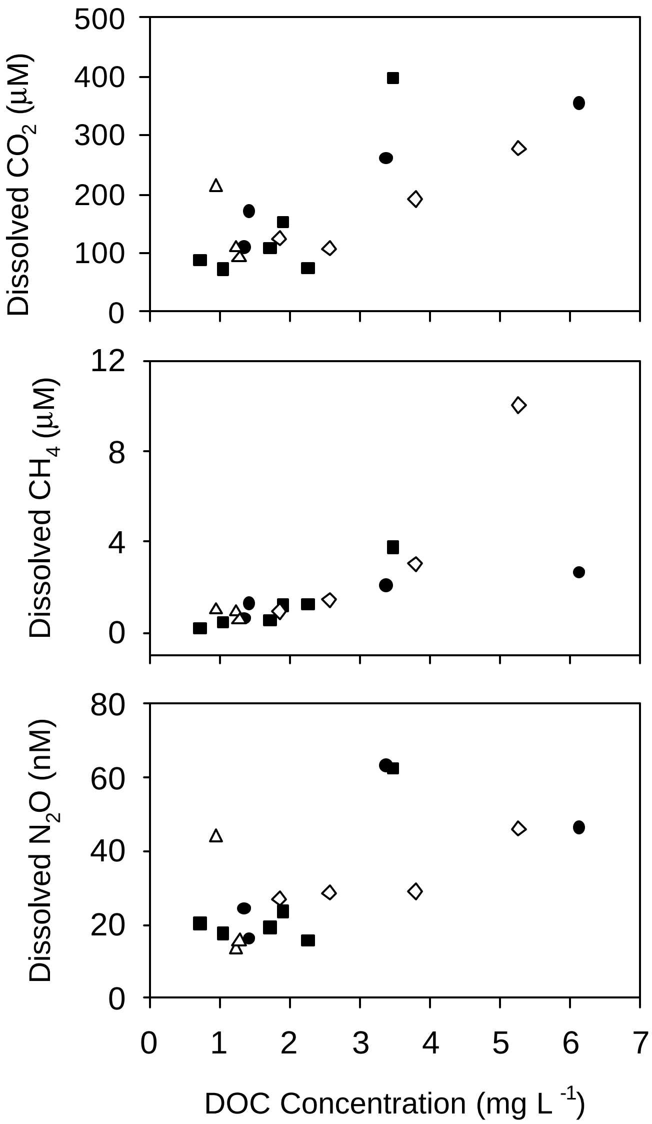

Figure 1. Mean DOC concentration vs. mean CO_2, CH_4, and N_2O concentrations in SFBR headwater streams. Symbols: ● - residential/developed; Δ - forested; € - mixed; • - pasture

and TDN levels (Table 1). Further, the stream which exhibited the highest individual N_2O concentrations, the highest mean CO_2 concentration, and the second highest mean CH_4 concentration (M78) had TDN concentrations that were no higher than those from streams draining other watersheds which contain a substantial amount of non-forest land use but do not exhibit elevated trace gas concentrations. These observations suggest that concentrations of N_2O and CH_4, which contain N and C that are at levels several orders of magnitude below those of TDN and DOC, may be sensitive indicators of organic and/or nutrient contamination that are at levels too low to be reflected by TDN and DOC. Our limited data suggest that N_2O concentrations above about 15 nM and CH_4 concentrations above about 1 µM in small steams of the Georgia Piedmont may indicate watershed contamination by nutrients and/or organic wastes. Thus, elevated trace gas concentrations may be useful indicators of incipient watershed impairment.

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